



# Novel nitrogen-doped hierarchically porous coralloid carbon materials as host matrixes for lithium–sulfur batteries



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## ABSTRACT

Nitrogen-doped hierarchically porous coralloid carbon/sulfur composites (N-HPCC/S) served as attractive cathode materials for lithium–sulfur (Li–S) batteries were fabricated for the first time. The nitrogen-doped hierarchically porous coralloid carbon (N-HPCC) with an appropriate nitrogen content (1.29 wt%) was synthesized via a facile hydrothermal approach, combined with subsequent carbonization–activation. The N-HPCC/S composites prepared by a simple melt–diffusion method displayed an excellent electrochemical performance. With a high sulfur content (58 wt%) in the total electrode weight, the N-HPCC/S cathode delivered a high initial discharge capacity of 1626.8 mA h g<sup>−1</sup> and remained high up to 1086.3 mA h g<sup>−1</sup> after 50 cycles at 100 mA g<sup>−1</sup>, which is about 1.86 times as that of activated carbon. Particularly, the reversible discharge capacity still maintained 607.2 mA h g<sup>−1</sup> after 200 cycles even at a higher rate of 800 mA g<sup>−1</sup>. The enhanced electrochemical performance was attributed to the synergetic effect between the intriguing hierarchically porous coralloid structure and appropriate nitrogen doping, which could effectively trap polysulfides, alleviate the volume expansion, enhance the electronic conductivity and improve the surface interaction between the carbon matrix and polysulfides.

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## 1. Introduction

Lithium–sulfur (Li–S) rechargeable batteries are drawing tremendous attention due to the great potential to satisfy the increasing demand of the imminent energy and environmental issues [1–3]. Sulfur is a promising cathode for the next-generation energy storage system to provide much higher energy density. At an operating potential of 2.1 V, sulfur cathode delivers a high specific capacity of 1675 mA h g<sup>−1</sup>, which gives Li–S batteries a specific energy of 2600 Wh kg<sup>−1</sup>, much higher than that of the current lithium-ion batteries [4–6]. In addition, sulfur is naturally abundant, low cost, and environmentally benign, which makes it attractive for large-scale practical applications.

Nevertheless, there are still several serious drawbacks of sulfur cathode, severely limiting the practical applications of Li–S batteries. (1) Low utilization of active materials due to the electrical insulating nature of sulfur ( $5 \times 10^{-30}$  S cm<sup>−1</sup> at 25 °C). (2) Poor cycling performance and low coulombic efficiency

resulting from the high solubility of intermediate products Li<sub>2</sub>S<sub>n</sub> (2 < n ≤ 8). (3) Structural collapse of sulfur cathode because of the large volume changes of sulfur particles during lithiation/delithiation [7,8].

Many approaches have been proposed to address these considerable challenges described above. The most widely used method to improve the utilization of sulfur and cycling stability is to host sulfur in porous carbon [9–11]. It can provide enough space for the volume changes of sulfur and suppress the diffusion of the dissolved polysulfides effectively on account of the porous structure, abundant porous channels and strong adsorbent properties [12]. Carbon hosts with various morphologies have been researched, for instance, carbon hosts with microporous [13,14], mesoporous [15,16], hollow nanofiber [17,18] and porous hollow sphere structures [19,20]. According to recent studies [21,22], the three-dimensional hierarchical porous carbon can not only facilitate Li ions transport by shortening diffusion pathways, but also generate essential electrical contact with sulfur and favor the storage of sulfur. Huang et al. [23] synthesized a three-dimensional hierarchical porous carbon as sulfur host, which played an important role in enhancing electrochemical performances of Li–S batteries. Zhang et al. [24] prepared a novel

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three-dimensional hierarchical porous honeycomb carbon for Li–S battery with effective trapping of polysulfides. Although the three-dimensional hierarchical porous carbon can enhance the cyclability of Li–S batteries, the adsorption ability and electronic conductivity are relatively poor compared with other porous carbons modified with heteroatom. It is noted that nitrogen atom is the most attractive heteroatom, which can substantially improve the carbon wettability, adsorption ability, surface polar and electronic conductivity [25]. Furthermore, nitrogen doping can assist the carbon matrix to inhibit the diffusion of polysulfides by means of the enhanced interface adsorption and provide high initial discharge capacity of the carbon/sulfur composites [26]. Recently, nitrogen-doped one-dimensional porous carbons have attracted much attention for application in Li–S batteries. For example, Yang et al. [27] first proposed nitrogen-doped porous carbon nanofiber webs/sulfur composites, which displayed an excellent electrochemical performance. However, while the one-dimensional porous carbon has advantages of large electrode–electrolyte interfaces and favorable Li ions transport, its limited pore volume and low surface area limit the capability in accommodating sulfur. Inspired by previous studies, our group try to combine the advantages of three-dimensional hierarchical structure and nitrogen doping and fabricate carbon matrix by a simple method, which will serve as an advanced host for Li–S batteries.

In this work, nitrogen-doped hierarchically porous coraloid carbon/sulfur composites (N-HPCC/S) were first proposed. The N-HPCC was prepared by a simple process and the template used was low cost, which was significant to realize the commercial application of Li–S batteries. The obtained N-HPCC possessed a three-dimensional hierarchical nanostructure and appropriate nitrogen doping. Due to the special three-dimensional hierarchically porous coraloid nanostructure, the N-HPCC could effectively confine a relatively high amount of sulfur, suppress the dissolution of polysulfides and withstand volume variation. Furthermore, nitrogen doping could significantly enhance the electronic conductivity and increase the surface interaction between the carbon matrix and polysulfides [28,29]. It suggests that these structural and surface chemistry features working co-operatively are good strategies to achieve excellent electrochemical performances of Li–S batteries.

## 2. Experimental

### 2.1. Synthesis of N-HPCC

The aqueous solution containing 0.99 M  $\text{Mn}(\text{NO}_3)_2$  (15 mL) and 0.99 M aniline (10 mL) was continuously stirred for 15 min. Then 0.99 M  $\text{KMnO}_4$  (25 mL) aqueous solution was added dropwise to the homogeneous solution and the solution turned black immediately. The mixture was ultrasonically dispersed for 1 h

and then sealed into a Teflon-lined stainless steel autoclave. The autoclave was heated to 180 °C for 4 h, followed by natural cooling to room temperature. The precipitate was collected and dried at 60 °C for 12 h in a vacuum oven after being washed with deionized water and ethanol several times. Then, the obtained product was pre-carbonized at 400 °C for 2 h under  $\text{N}_2$  atmosphere. The resulting material and KOH (at a 1:0.5 mass ratio) were mixed by ultrasonic for 2 h and then dried at 80 °C. Afterwards, the dried solid sample was carbonized at 700 °C for 2 h under  $\text{N}_2$  atmosphere. Finally, the carbonized sample was etched by HCl (15 wt%) to generate N-HPCC.

### 2.2. Synthesis of N-HPCC/S

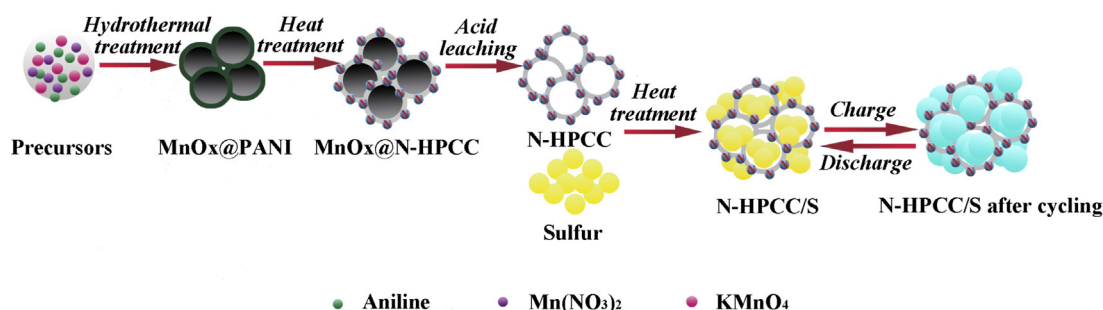
The N-HPCC/S composites were prepared via a simple melt-diffusion method. Typically, the N-HPCC was mixed with sublimed sulfur in a quartz mortar with different weight ratios of 1:1.4, 1:2 and 1:3 (denoted as N-HPCC/S-1, N-HPCC/S-2 and N-HPCC/S-3), and ground for 1 h into uniformity. Then, these composites were separately put into three sealed Teflon containers for 12 h at 155 °C under argon condition to ensure that the melting sulfur could diffuse into the pores of the N-HPCC easily. The schematic illustration of preparing N-HPCC/S is shown in Scheme 1.

### 2.3. Materials Characterization

The morphological characterizations of the powders were investigated with the Hitachi-S4800 Scanning electronic microscope (SEM) and transmission electronic microscope (TEM) with model JEM2010. Thermogravimetric Analysis (TGA) apparatus (Pyris Diamond, PerkinElmer Thermal Analysis) was conducted to determine the sulfur content in the composites under nitrogen flow. X-ray diffraction (XRD) patterns were obtained using a Rigaku D/MAX-2500/pc. Nitrogen adsorption-desorption isotherms were measured at 77 K with an ASAP 3000 adsorption analyzer (Micromeritics). The Brunauer–Emmett–Teller (BET) method was utilized to calculate the specific surface areas. Pore size distribution (PSD) was derived from the adsorption branch of the isotherms using the Barrett–Joyner–Halenda (BJH) model. Total pore volumes were calculated from the amount adsorbed at a relative pressure  $P/P_0$  of 0.994. X-Ray photoelectronic spectroscopy (XPS) measurements were carried out on a Kratos XSAM-800 spectrometer with Al  $K\alpha$  radiation source. High-resolution spectra of the individual elements were collected with the analyzer pass energy set at 20 eV. During all XPS experiments, the pressure inside the vacuum system was maintained at  $1 \times 10^{-9}$  Pa.

### 2.4. Electrochemical measurements

The cathode consisted of 80 wt% active materials, 10 wt% acetylene black, and 10 wt% polyvinylidene fluoride (PVDF) binder.



**Scheme 1.** Schematic illustration of the synthesis procedure of the N-HPCC/S.

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